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IN RECOVERY FURNACES**

K.M. NICHOLS, L.M. THOMPSON, AND H.J. EMPIE

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A REVIEW OF NO_x FORMATION MECHANISMS IN RECOVERY FURNACES

Kenneth M. Nichols, Laura M. Thompson, and H. Jeff Empie
The Institute of Paper Science & Technology
575 14th Street N. W.
Atlanta, Ga. 30318

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ABSTRACT

Review of NO_x formation studies shows that NO forms in recovery furnaces primarily by two independent mechanisms; thermal, and fuel. Thermal NO formation is extremely temperature sensitive; theoretical predictions show the potential for thermal NO to increase dramatically with moderate increases in recovery furnace temperature. Fuel NO formation is relatively temperature insensitive, and is related to fuel nitrogen content. Black liquors are shown to contain 0.04 to 0.26 weight percent fuel nitrogen. Conversion of just 20% of this would yield approximately 20-130 ppm NO (at 8% O₂) in the flue gas, enough to represent a significant portion of the total NO. Data from operating recovery furnaces show NO_x emissions ranging from near zero to over 100 ppm (@ 8% O₂); much lower than emissions from coal, oil, and gas combustion. An apparent increase in recovery furnace NO_x emissions was observed with increasing solids. This increase is much less than predicted by thermal NO formation theory, indicating that other NO formation/destruction mechanisms are important. No data are available to show the relative importance of thermal and fuel NO to total NO_x during black liquor combustion. These data are necessary to understand the impact of increases in solids concentration (and accompanying increases in combustion temperatures) on recovery furnace NO_x emissions, since the temperature dependency is not the same for each mechanism.

KEYWORDS

nitrogen oxides, recovery furnaces, emissions, combustion, kinetics, mechanism, high solids, fume

INTRODUCTION

Nitric oxide (NO) and nitrogen dioxide (NO₂) are formed during combustion whenever nitrogen is present in the fuel or in the combustion air. These oxides of nitrogen (collectively referred to as NO_x) are considered to be key constituents in reactions associated with photochemical smog and acid rain (1). For these reasons NO_x emissions from stationary combustion sources have been regulated by local and federal agencies.

Traditionally, recovery furnaces have been operated such that NO_x emission levels were well below typical emission standards. Surveys of NO_x emissions from kraft recovery furnaces in the late 70's (2,3) showed emissions in the range 0.05 to 0.14 pounds per million BTU (26 to 71 ppm on an in-stack concentration basis). At the same time, the emissions standard for oil-fired steam generators was 0.30 pounds NO_x per million BTU.

More recently, due to improved technologies for concentrating black liquors, recovery furnaces are operating at higher levels of liquor solids concentration. Decreases in liquor moisture will result in higher combustion temperatures, and there is some concern that increased temperatures will yield increases in NO_x emissions. In several cases, observed increases in recovery furnace NO_x emissions have been related to firing higher solids concentrations (4-7).

The purpose of this paper is to present basic information on the chemistry and formation of NO_x that has been developed in other combustion fields (such as fossil fuel combustion), to discuss the implications for NO_x emissions from

recovery furnaces, and to identify several research needs relating to the subject of recovery furnace NO_x emissions.

MECHANISMS FOR NO_x FORMATION

Most of the NO_x emitted by combustion sources is NO with only a small fraction (typically 5% or less) appearing as NO_2 . The total NO emitted is formed by three independent mechanisms: thermal NO (the fixation of molecular nitrogen by oxygen atoms produced at high temperatures), fuel NO (the oxidation of nitrogen contained in the fuel during the combustion process), and prompt NO (the attack of hydrocarbon free radicals on molecular nitrogen producing NO precursors). Prompt NO is usually considered to be of minor importance for industrial furnaces (8). The relative importance of each of the other two mechanisms in determining the total NO emission level is dependent on furnace temperatures and fuel nitrogen levels.

The kinetics involved in these NO formation mechanisms are generally rate limiting. Concentrations of NO measured in hot combustion gases are typically orders of magnitude less than equilibrium concentrations at hot gas temperatures. Conversely, NO levels are effectively frozen as the combustion gases are cooled, resulting in flue gas concentrations which are much greater than equilibrium concentrations at low temperatures.

Thermal NO

Thermal NO is the dominant source of NO emissions for combustion of fuels such as natural gas which contain very low levels of nitrogen. The

mechanism for the formation of thermal NO was first described by Zeldovich (9) in 1946 as the two reaction steps



The first step (Reaction 1) is rate-limiting and has a very high activation energy (75 kcal/gmol). This high activation energy implies that high temperatures are required for significant NO formation, hence the designation "thermal" NO. The Zeldovich mechanism is frequently extended (8) to more accurately describe thermal NO formation under fuel-rich conditions by including a third reaction step



Because thermal NO is formed during the combustion of nearly all fuels, this mechanism has been studied extensively. Kinetic rate coefficients for both the forward and reverse rates (of Reactions 1-3) have been reported over a wide range of temperatures (10). The reactions involve primarily the oxygen-nitrogen system and can be, with reasonable accuracy, considered separately from the combustion process, since the time scale for NO formation reactions is generally greater than the time scale for combustion reactions. This allows the information derived from laboratory combustion studies to be applied to thermal NO formation in industrial furnaces.

From the Zeldovich mechanism (Reactions 1 and 2), a simple expression can be derived to approximate the rate of thermal NO formation. In practical

flames, NO concentrations are small compared to O₂ and N₂ concentrations, and the forward rates are greater than the reverse rates. Considering only the forward reactions, and invoking the steady state assumption for atomic nitrogen (i.e., $d(N)/dt = 0$), the following expression is obtainable

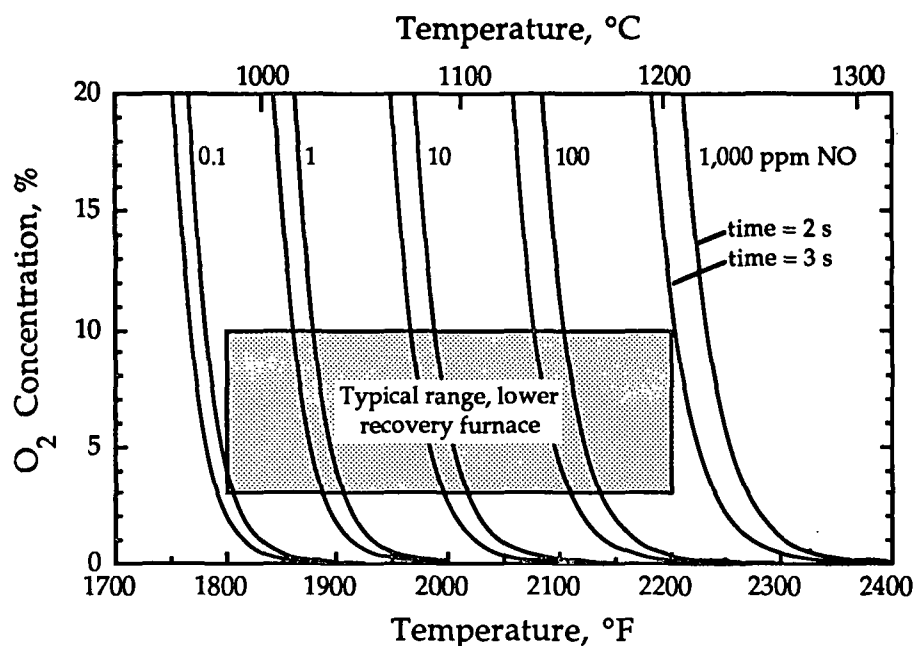
$$\frac{d(NO)}{dt} = 2k_1 (O) (N_2) \quad (4)$$

where k_1 is the rate constant for the forward rate of Reaction 1. By assuming equilibration of the combustion reactions, the concentration of atomic oxygen can be estimated from its equilibrium with O₂. As shown by Bowman (10), substitution of generally accepted expressions for both the equilibrium concentration of atomic oxygen, and for the forward rate constant, k_1 , into Equation 4 yields

$$\frac{d(NO)}{dt} = \frac{1.44 \times 10^{20}}{T^{1/2}} \exp [-69,500 / T] (O_2)^{1/2} (N_2), \text{ kgmol/m}^3/\text{s} \quad (5)$$

where T is gas temperature in Kelvins, t is reaction time in seconds, and all gas concentrations are in units of kgmol/m³. It is evident from this rate expression that thermal NO formation is highly temperature dependent, and is also dependent on oxygen concentration and residence time. This is more clearly illustrated with Figure 1, which is a graphical representation of Equation 5. Figure 1 shows the potential for moderate increases in temperature to have a significant impact on thermal NO formation.

1. Approximate temperature and oxygen dependency of thermal NO, as determined by Equation 5 for residence times of 2 and 3 seconds.



Concentrations of thermal NO increase by an order of magnitude for each 100-140 $^{\circ}F$ (55-80 $^{\circ}C$) increase in furnace temperature. The dependencies on oxygen concentration and residence time are less pronounced than the temperature dependency.

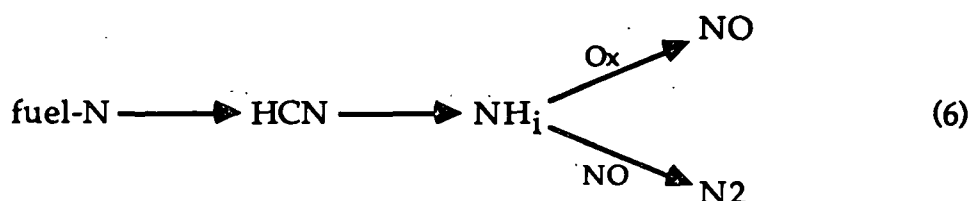
Comparison of the predicted thermal NO formation with the typical ranges of oxygen and temperature in the lower recovery furnace shows that thermal NO formation is appreciable only in those areas of the recovery furnace where the highest average temperatures exist. This suggests that the region of primary air sweeping across the char bed surface may be the key region (or at least one of the key regions) in the furnace for production of thermal NO.

The relative importance of thermal NO cannot be determined from Figure 1, since the ranges of recovery furnace operating conditions and the thermal NO predictions are only approximations.

Figure 1 and Equation 5 also illustrate that strategies for reducing thermal NO formation must bring about reductions in one or more of furnace temperatures, oxygen concentrations, or residence times at high temperature. As discussed by Anderson and Jackson (11), demonstrated strategies include biased firing, off-stoichiometric combustion (or air staging), and low excess air firing.

Fuel NO

Fuel NO is formed during combustion as a result of the oxidation of nitrogen contained in the fuel. A great deal of research has been focused on understanding the elementary steps and reaction mechanisms leading from fuel nitrogen to fuel NO. General reviews of this research are available (12, 13). A large number (hundreds) of reactions are involved, and many of these contain difficult-to-measure intermediates and radical species. Though an exact determination of the complete mechanism is presently not available, it is generally accepted (10, 13-15) that the fuel NO mechanism includes a rapid (not rate limiting) conversion of fuel nitrogen compounds into intermediate nitrogen compounds (HCN, CN, NH_2 , NH, N) which can either be converted to NO by attack of oxygen containing species or be converted to N_2 by reaction with NO itself. This is often represented by an overall reaction pathway as



Overall reaction rates of NO and N₂ formation from fuel nitrogen have been determined for laboratory hydrocarbon flames doped with simple nitrogen compounds such as ammonia, cyanogen, and pyridine (14, 15). These overall reaction rates measured on simpler combustion systems have been applied with encouraging success for the prediction of fuel NO formation during coal combustion (16).

Factors affecting fuel NO formation are fuel nitrogen content and concentration of oxygen in the gas. Unlike thermal NO, the formation of fuel NO is relatively insensitive to temperature changes caused by changes in air preheat or changes in fuel heating value (17). Increased fuel nitrogen content can lead to higher emissions of fuel NO, although fuel NO cannot be correlated with nitrogen content alone. The relationship between weight percent of nitrogen in fuel, and the percent of fuel nitrogen conversion to NO in practical combustors has been reported for a variety of fossil and synthetic fuels with nitrogen contents up to 2% (1, 10). On average, fractional conversion to NO increases with decreasing nitrogen content. The data, however, are widespread; for example, fuels containing less than 0.2% nitrogen showed conversions to NO ranging from a minimum of 20% to as high as 80%.

There are little to no data showing the fractional conversion of black liquor nitrogen to NO. Researchers investigating nitrogen dioxide pretreatment of pulp (the Prenox process) found that 5% or less of the nitrogen in nitrate added to black liquor was found as NO_x in the recovery boiler flue gases (18). This may not be representative, however, since the inorganic form of the nitrogen bound in nitrate may behave very differently than the chemical forms of nitrogen found in black liquor.

Measurements of nitrogen content for a number of kraft black liquors are shown in Table I. Expressed as a weight percentage of the dry liquor solids, the values are in the range 0.04-0.26 with the average being 0.12. Using the minimum fuel nitrogen to NO conversion value of 20% discussed above, a recovery furnace burning black liquor with the range of nitrogen contents in Table I would yield NO emission levels of approximately 20-130 ppm in the flue gas (@ 8 % O₂). This estimate suggests that fuel nitrogen is an important source of recovery furnace NO_x.

Additional support for this is provided by residual oil combustion studies (19). Fuel NO was shown to be responsible for greater than 50% of total NO emissions during residual oil combustion at conditions of high air preheat (530 °F) and about 80% of total NO without air preheat (because thermal NO was lower). The residual oil contained 0.20% nitrogen, which is within the range of black liquor nitrogen values shown in Table I.

I. Nitrogen levels in thirteen kraft black liquors.

<u>Mill</u>	<u>wood</u>	<u>N, % of dry solids</u>
1	mx	0.05
2	sw	0.06
3	sw	0.06
4	mx	0.06
5	sw	0.1
6	NA ^a	0.1
7	NA	0.14, 0.15 ^b
8	NA	0.04, 0.05 ^b
9	NA	0.14, 0.14 ^b
10	NA	0.23, 0.26, 0.20, 0.19, 0.08, 0.07 ^b
11	NA	0.12, 0.11, 0.21, 0.18, 0.10, 0.10 ^b
12	NA	0.1
13	NA	0.1
Average		0.12
Standard Dev.		0.06

a not available

b samples collected on different days

A question of importance to fuel NO formation is during which stage of combustion the fuel nitrogen is released (or converted) from its chemical form in the fuel to the gas phase intermediates in Equation 6. This will affect when and where in the furnace the reaction of the intermediates will occur, and will affect the distribution of products formed (i.e., NO versus N₂). In combustion of coal, the release of fuel nitrogen occurs primarily during devolatilization, although additional nitrogen release occurs during char combustion (20). Thus, the majority of the coal nitrogen is chemically bound in a manner so as to be readily volatile.

For coals, the rate at which nitrogen is released is normally slightly more rapid (by a factor of 1.2-1.5) than the rate at which carbon is burned from the

fuel. The chemical form of nitrogen in coal is thought to be primarily heterocyclic aromatic ring structures such as pyridine, though this is difficult to ascertain, since removal of the nitrogen containing compounds from coal without their destruction is difficult. There are no data available for black liquor to show the chemical form of the fuel nitrogen, or to show how much is released during the respective stages of devolatilization and char burning.

RECOVERY FURNACE EMISSIONS

Published data on NO_x emissions from recovery furnaces are somewhat limited. Table II provides a summary of reported NO_x emissions along with the sources of the data. Emission levels (adjusted to a common basis of ppm at 8% O_2 in flue gas) range from near zero to over 100 ppm. These emissions are relatively low when compared to NO_x emissions from coal, oil, and gas fired furnaces (21, 22) and illustrate why NO_x emissions from recovery furnaces have not been given as much consideration as NO_x emissions from other combustion sources.

By considering those data in Table II for which liquor solids concentrations are available, a trend is apparent. These data (plotted in Figure 2) suggest that NO_x levels increased approximately four fold as solids increased from 62 to 77%. Some useful implications result from comparing this observed increase to that predicted for thermal NO formation. Integration of Equation 8 shows that for given values of O_2 and N_2 concentrations, temperature, and residence time, a four fold increase in thermal NO would require approximately a 40 °C increase in temperature. Yet it is likely that furnace temperatures increased by much more than 40°C for an increase in solids from 62 to 77%. Theoretical

II. Summary of published NO_x flue gas concentrations from kraft and NSSC recovery furnaces.

<u>Source</u>	<u>% solids</u>	<u>(NO_x), units as reported</u>	<u>(NO_x), ppm @ 8% O₂</u>
Galeano and Leopold (1971)	NA ^a	0-53 ppm	33
Galeano and Leopold (1971) ^b	NA	13-65 ppm	35
Galeano, et al. (1973) ^b	62	10-50 ppm	30
Hood and Miner (1981)	NA	0.05-0.14 lb/10 ⁶ BTU (data from 10 furnaces)	20-55 ^c
Bjorklund, et al. (1989)	64.6 ^d	95 ppm	73
Bjorkland, et al. (1989)	76.5 ^d	155 ppm	120
Brannland, et al. (1990)	65.0	57 mg/MJ	60
Casale & Fritz (1990)	74.0	77 ppm (emission limitation)	77
Anderson and Jackson (1991)	NA	80 ppm (emission limitation)	80
IPST data (1991)	67.6 ^d	70 ppm ^e	59
IPST data (1991)	67.9 ^d	110 ppm ^e	91

a not available

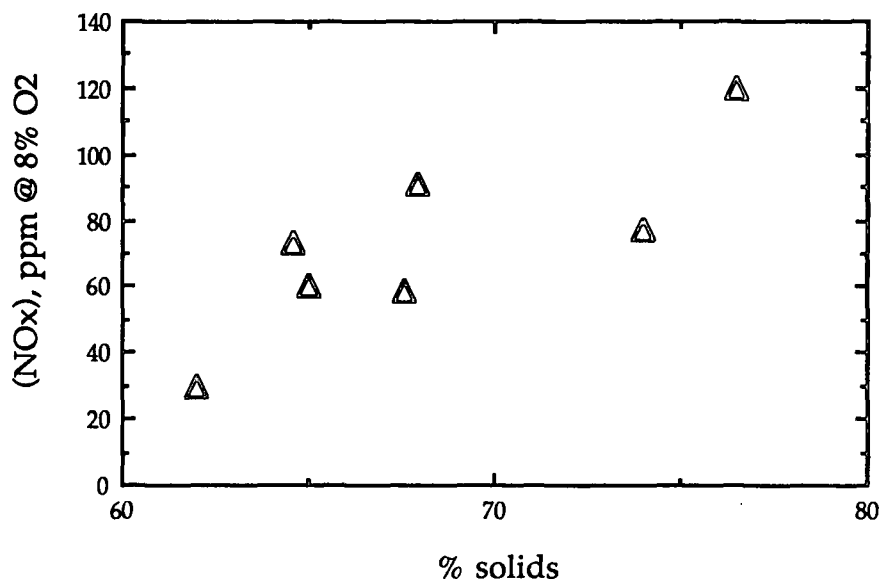
b NSSC liquor

c based on approximate conversion factor of (390 ppm @ 8% O₂)/(lb/10⁶ BTU)

d before salt cake addition

e represents average of 6 to 10 one day tests

2. NO_x emissions observed in flue gases from recovery furnaces, effect of increasing solids, all values normalized to a common basis of 8% O_2 in flue gas, sources of data as given in Table II.



flame temperature estimations for black liquor combustion (23) show a 230 °C temperature increase over this range. Equation 5 and Figure 1 show an increase of thermal NO by a factor of several hundred for a 230 °C temperature increase.

The fact that the observed temperature dependency is much less than approximated by thermal NO formation theory suggests that mechanisms other than thermal NO formation play an important role in determining recovery furnace NO_x emissions. Two possibilities are: 1) a substantial portion of the total recovery furnace NO originates as fuel NO which is not temperature sensitive, and 2) NO destruction reactions are occurring and

tending to mask or partially mask the temperature dependency. The first of these possibilities has been discussed above. The second is discussed below.

NO_x DESTRUCTION REACTIONS

Levels of NO emissions depend not only on the rate of formation of NO, but also on the rate of destruction. Once NO is formed, it can be partially destroyed before leaving the furnace. Measurements of NO profiles as a function of distance from the flame have been made in several instances (20, 24) in laboratory and pilot scale combustion. Results showed that NO is rapidly formed and then slowly destroyed. Concentrations pass through a maximum in or near the flame zone and undergo reduction in the post flame gases. The effluent or flue gas concentration does not necessarily represent the maximum level of NO concentration formed in the furnace. The reduction can be up to 50% or more of the maximum level reached in the furnace, with fuel rich flames and particle laden flames giving the most destruction, and fuel lean and homogeneous flames giving less destruction (24, 25).

This NO reduction is due partially to gas phase reaction of NO with nitrogen containing intermediates to form N₂ (as shown in Equation 6). The fact that the extent of NO reduction is greater in coal combustion than in gas or liquid combustion (25) showed that char and ash species are also responsible for NO reduction. Kinetic rates of reduction of NO to N₂ by chars have been measured (24-26). Rate expressions are generally reported in the form

$$\frac{-d(\text{NO})}{dt} = A \exp [-E/(RT)] A_E (\text{NO}). \quad (7)$$

showing the dependence on char external surface area (A_E), NO concentration, temperature, and residence time.

Returning to the apparent trend in Figure 2, it is possible that NO formation in the recovery furnaces increased by much more than four fold as solids increased from 62 to 77%, but that NO destruction due to air staging served to counter or dampen the increase such that only some of the increase was seen in flue gases. As discussed by Galeano and Leopold (21), the conventional kraft recovery furnace, in order to promote formation of sulfide, uses the concept of air staging which is coincidentally a proven method for reducing NO emissions from utility boilers. Less than stoichiometric air in the lower furnace will decrease thermal NO formation by decreasing concentrations of atomic oxygen, and will decrease conversion of fuel nitrogen to NO while increasing conversion to N_2 (as indicated by the overall pathway shown in Equation 6).

A destruction mechanism which may be especially important in recovery furnaces is the reaction of NO_x with fume species. Fume particulates represent a tremendously large surface area for reactions with gas phase species. Sulfur gases including oxides of sulfur are known to react with fume species. Oxides of nitrogen may also undergo similar reducing reactions. Several possible reactions of nitrogen oxides with sodium species have been suggested (27) based on thermodynamic feasibility. If such reactions are occurring, burning black liquor at higher solids concentrations and higher

combustion temperatures may serve to increase the fuming rate, and increases in fume-NO_x interactions would counter the increases in thermal NO formation.

CONCLUSIONS AND RESEARCH NEEDS

Recovery furnace NO_x is formed primarily by thermal and fuel NO formation mechanisms. Little to no data are available to show the relative importance of each in black liquor combustion. This is an important question to answer and identifies a strong research need since the temperature dependence is very different for each mechanism.

Thermal NO is highly temperature sensitive. Theory predicts that moderate increases in furnace temperature (100-140 °F or 55-80 °C) will yield order of magnitude increases in thermal NO concentrations. Due to this sensitivity, it can be concluded that the zones in the recovery furnace controlling thermal NO formation are those of highest average temperature.

Fuel NO is relatively temperate insensitive, and thus fuel NO in recovery furnaces is not expected to be affected by increasing solids concentrations. Black liquor solids contain 0.04 to 0.26 weight percent nitrogen, which represents a significant potential for fuel NO formation. The fact that fuel NO accounts for the majority of total NO in combustion of residual fuel oil containing nitrogen at a similar level to black liquors (0.2%) also suggests that fuel NO may be important in recovery furnaces.

No information is available concerning the chemical form of nitrogen in black liquors, or concerning how much is released during devolatilization versus during char combustion. This identifies a second research need, as this will affect when and where in the furnace the fuel nitrogen is released and will affect the relative distribution of NO and N₂ formed.

Published NO_x emissions data from operating recovery furnaces show values of near zero to over 100 ppm (@ 8% O₂), which are much lower than typical values from coal, oil, and gas combustion. The data show approximately a four fold increase in NO_x as solids increased from 62 to 77%. This increase is much less than predicted by the temperature dependence of thermal NO theory, suggesting the possibility that NO destruction reactions are occurring in recovery furnaces. This identifies a third area of research need, to evaluate the impact of potential NO_x destroying mechanisms.

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